



Preliminary communication/Communication

Dimeric and monomeric palladium(II) parent-amido (NH₂) complexes: Synthesis, characterization, and reactivity



Youngwon Kim, Soonheum Park*

Department of Chemistry, Dongguk University–Gyeongju, 123 Dongdae-ro, Gyeongju, Gyeongbuk, Republic of Korea

ARTICLE INFO

Article history:

Received 6 April 2015

Accepted after revision 11 May 2015

Available online 15 July 2015

Keywords:

Parent–amido palladium

C–N bond formation

Syn-insertion

Diastereospecific insertion of the C≡C into

the Pd–N bond

X-ray crystal structure

ABSTRACT

The treatment of [PdL₃(NH₃)]OTf (L₃ = (PEt₃)₂(Ph) (**1**), (2,6-(Cy₂PCH₂)₂C₆H₃) (**3**)) with NaNH₂ in THF afforded dimeric and monomeric parent-amido palladium(II) complexes with bridging and terminal NH₂, respectively, *anti*-[Pd(PEt₃)(Ph)(μ-NH₂)₂] (**2**) and Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₂) (**4**). The dimeric complex **2** crystallizes in the space group *P*2₁/*n* with *a* = 13.228(2) Å, *b* = 18.132(2) Å, *c* = 24.745(2) Å, β = 101.41(1)°, and *Z* = 4. It has been found that there are two crystallographically independent molecules with Pd(1)–Pd(2) and Pd(3)–Pd(4) distances of 2.9594 (10) and 2.9401(9) Å, respectively. The monomeric amido complex **4** protonates from trace amounts of water to give the cationic ammine species [Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₃)]⁺. Complex **4** reacts with diphenyliodonium triflate ([Ph₂I]OTf) to give aniline complex [Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₂Ph)]OTf (**5**). Reaction of **4** with dialkyl acetylenedicarboxylate (DMAD, DEAD) yields diastereospecific palladium(II) vinyl derivative (*Z*)-[Pd(Cy₂PCH₂)₂C₆H₃](CR = CR(NH₂)) (R = CO₂Me (**6a**), CO₂Et (**6b**)). Reacting complexes **6a** and **6b** with *p*-nitrophenol produces (Pd(Cy₂PCH₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (**8**) and *cis*-CHR = CR(NH₂), exclusively.

© 2015 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

Amido complexes of late transition metals are of incessant interest because of potential applications for catalysis, involving the formation of carbon–nitrogen bonds [1,2]. Most recent studies have been focused on such complexes containing an arylamido ligand that may stabilize the metal–amido bond by partially delocalizing the electron density on the amido nitrogen to an aryl-substituent [2]. However, such complexes with a parent-amido ligand (NH₂) have been relatively little explored [1,3–5]; nevertheless, such species are of importance as intermediates in metal-catalyzed amination reactions with ammonia [6]. Although palladium is the primary metal used in homogenous catalysis, there are a few

examples of parent–amido complexes with this metal [6a,7].

Monomeric amido complexes have a strong affinity to undergo substitutional dimerization or oligomerization, particularly crucial for coordinatively unsaturated complexes, yielding amido-bridged species. We have previously reported monomeric dimethylamido and arylamido complexes of Pd(II) and Pt(II) having a phenyl substituted PCP pincer ligand [8]. Herein, we report the synthesis of dimeric and monomeric parent–amido complexes of palladium(II), in which the latter employs a sterically hindered cyclohexyl derivative of PCP pincer to preclude undergoing substitutional dimerization. Thus, the monomeric amido complex displays unique reactivity towards activated acetylenes via the insertion of carbon≡carbon triple bonds into the Pd–NH₂ bond to produce diastereospecific aminated vinyl palladium(II) complexes. Further reaction of the vinyl complexes with acidic phenol to liberate diastereoselective amino olefin derivatives is

* Corresponding author.

E-mail address: shpark@dongguk.ac.kr (S. Park).

described in terms of absolute diastereomeric configuration of the vinyl complex along with the reactivity feature in the ligand exchange reaction involving the σ -vinylic and the σ -phenoxide in the Pd(II) complexes.

2. Results and discussion

2.1. NH_2 -bridged dimeric amido complex

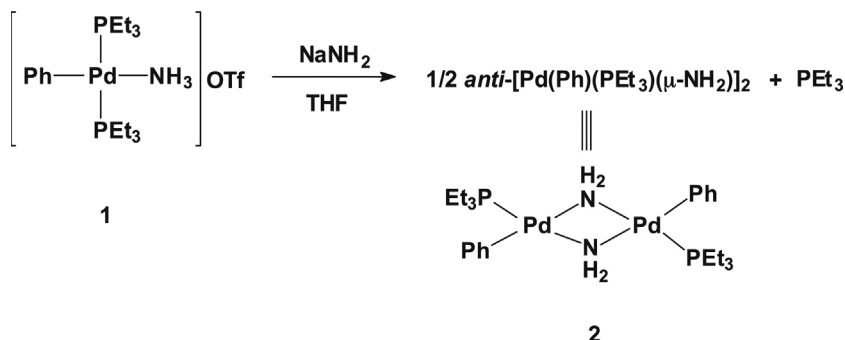
The reaction of a THF solution of *trans*-[Pd(PEt₃)₂(Ph)(NH₃)]OTf (**1**) with NaNH₂ at ambient temperature gives a gray suspension containing a single compound of palladium(II) along with dissociated triethylphosphine, evidenced by the ³¹P{¹H} NMR spectroscopy (Scheme 1). A pure off-white palladium(II) dimer *anti*-[Pd(PEt₃(Ph)(μ -NH₂))₂] (**2**) was obtained from a *n*-pentane extract of the residues resulted from the reaction mixture. The ³¹P{¹H} NMR spectrum of **2** in *d*₆-benzene shows a single peak at δ 20.2 indicative of a single compound in solution. In the ¹³C{¹H} NMR spectrum, the methylene carbon directly attached to the phosphorus resonates at δ 15.61 (¹J(CP) = 26.7 Hz) as a doublet. In the ¹H NMR spectrum, the bridged-amide protons (μ -NH₂) have been observed at δ -1.35 as a broad signal. The microanalytical data for **2** is consistent with dimeric formulation as was judged by NMR spectroscopic data.

Single crystals suitable for an X-ray diffraction study were obtained by slow evaporation of an *n*-pentane solution of *anti*-[Pd(PEt₃(Ph)(μ -NH₂))₂] (**2**). The molecular structure of one of the two crystallographically independent, but chemically identical molecules of **2** is shown in Fig. 1 [9]. The two independent molecular structures of **2** contain respective Pd₂N₂ rings puckered with dihedral angles of 53.1(2)° and 55.2(2)°. The Pd–Pd distances are 2.9594(10) and 2.9401(9) Å, respectively, indicating no bonding between the Pd–Pd [10], which are comparable with the Pt–Pt distances in the range of 3.087–3.134 Å found in the NH₂-bridged platinum(II) dimers, *anti*-[Pt(POPh₂)(PMePh₂)(μ -NH₂))₂] [4b], [Pt(PMe₂Ph)₂(μ -NH₂))₂]²⁺ [4c], and *anti*-[PtMe(PPh₃)(μ -NH₂))₂] [5a]. The Pd–N bond lengths are in the range of 2.067(7)–2.127(7) Å. The Pd–N–Pd and N–Pd–N bond angles are 88.8(3)–90.4(3)° and 77.7(3)–78.3(3)°, respectively. The dimeric complex **2** is intact to air and moisture. No reactions of **2** with unsaturated molecules such as CO₂, CH₂ = CHCN, dimethyl acetylenedicarboxylate (DMAD), diethyl maleate, and

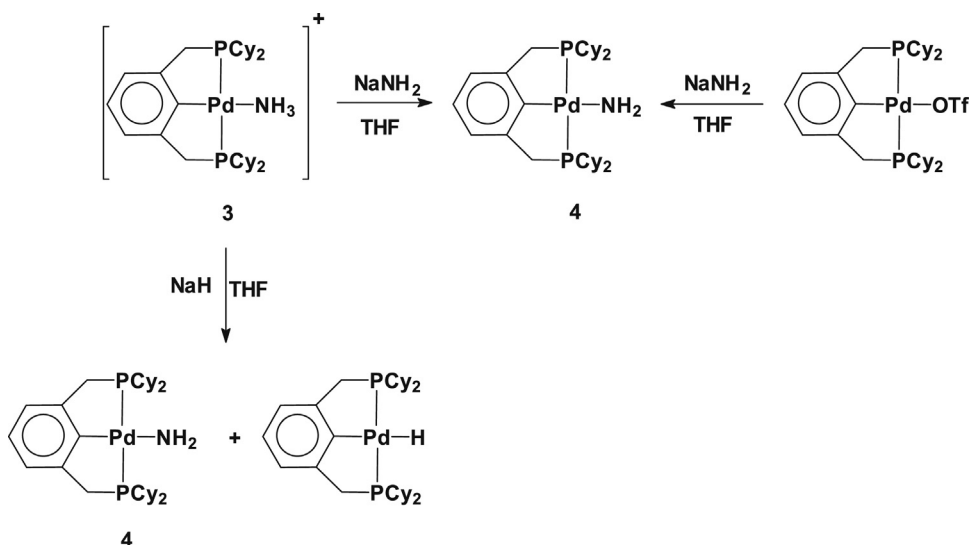
cyclohexene have been observed, revealing a lack of nucleophilicity on the part of the bridging NH₂. Taking into account the observed stability of **2**, it is rather unexpected that complex **2** is, to the best of our knowledge, the first structurally determined NH₂-bridged palladium(II) dimer (precedents of structurally determined bridging arylamido complexes of palladium(II) [11]), although a few precedents of analogous platinum(II) dimers have been reported [4,5a].

2.2. Monomeric amido complex

Since the formation of amide-bridged dimeric species resulted from substitutional dimerization by releasing triethylphosphine, we have used a palladium(II) ammine complex containing a *trans*-spanning terdentate ligand as a synthetic precursor for the preparation of a monomeric palladium(II) amide. Using the similar synthetic manner as for **2**, treatment of the cationic ammine complex [Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₃)](OTf) (**3**) with NaNH₂ afforded the monomeric amido complex Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₂) (**4**). When NaH was employed in place of NaNH₂ as a deprotonating agent, the reaction yields a mixture of two products including mainly the complex **4** along with a small amount of palladium(II) hydride (2,6-(Cy₂PCH₂)₂C₆H₃)PdH (the formation of the palladium(II) hydride (2,6-(Cy₂PCH₂)₂C₆H₃)Pd–H can be verified by observation of the upfield hydride resonance at δ -3.73 t (²J(PH) = 16 Hz) in the ¹H NMR spectrum [8b,12]). Alternatively, the metathetical replacement of the triflate ligand in (Pd(Cy₂PCH₂)₂C₆H₃)(OTf) with NaNH₂ exclusively yields the monomeric palladium(II) amide. The utilized synthetic routes are depicted in Scheme 2. The formation of Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₂) (**4**) was verified by the upfield shift NH₂ resonance at δ -0.20, and the relative intensity of the methylene protons in the pincer ligand and NH₂ resonances in the ¹H NMR spectrum. On dilution of a *d*₆-benzene solution of **4**, the NH₂ resonance shifts upfield, implicating an intermolecular hydrogen bonding in the complexes. Complex **4** is highly air and moisture sensitive. When the complex is exposed to a moisturized atmosphere or trace amounts of water, it immediately protonates to convert into the cationic ammine species [Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₃)]⁺, which was established by the observation of the identical ³¹P{¹H} NMR resonance with complex **3** at δ 52.7 in *d*₆-benzene (Scheme 3).



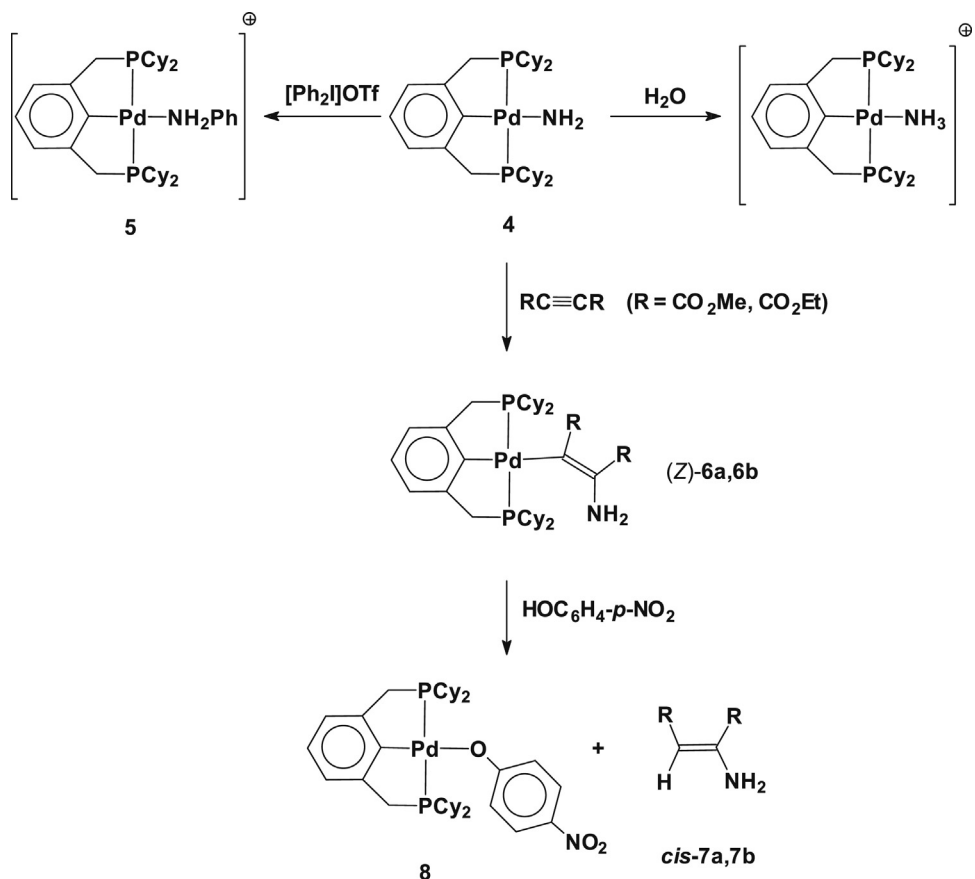
Scheme 1. Synthesis of *anti*-[Pd(PEt₃(Ph)(μ -NH₂))₂] (**2**).

Scheme 2. Synthesis of $(2,6-(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Pd}(\text{NH}_2)$ (**4**).

A d_6 -benzene solution of **4** reacts with diphenyliodonium triflate ($[\text{Ph}_2\text{I}]\text{OTf}$) to give the *N*-phenylated amine complex $[(2,6-(\text{PCy}_2)_2\text{C}_6\text{H}_3)\text{Pd}(\text{NH}_2\text{Ph})]\text{OTf}$ (**5**) (Scheme 3). The formation of the cationic aniline complex **5** can be verified by its independent preparation from the reaction of

$(2,6-(\text{PCy}_2)_2\text{C}_6\text{H}_3)\text{Pd}(\text{OTf})$ with NH_2Ph in d_6 -benzene (see [Experimental section](#)).

The monomeric amido complex **4** undergoes clean reactions with activated acetylene such as dialkyl acetylenedicarboxylate ($\text{RC}\equiv\text{CR}$; $\text{R} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$) to produce

Scheme 3. Reactions of $(2,6-(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Pd}(\text{NH}_2)$ (**4**).

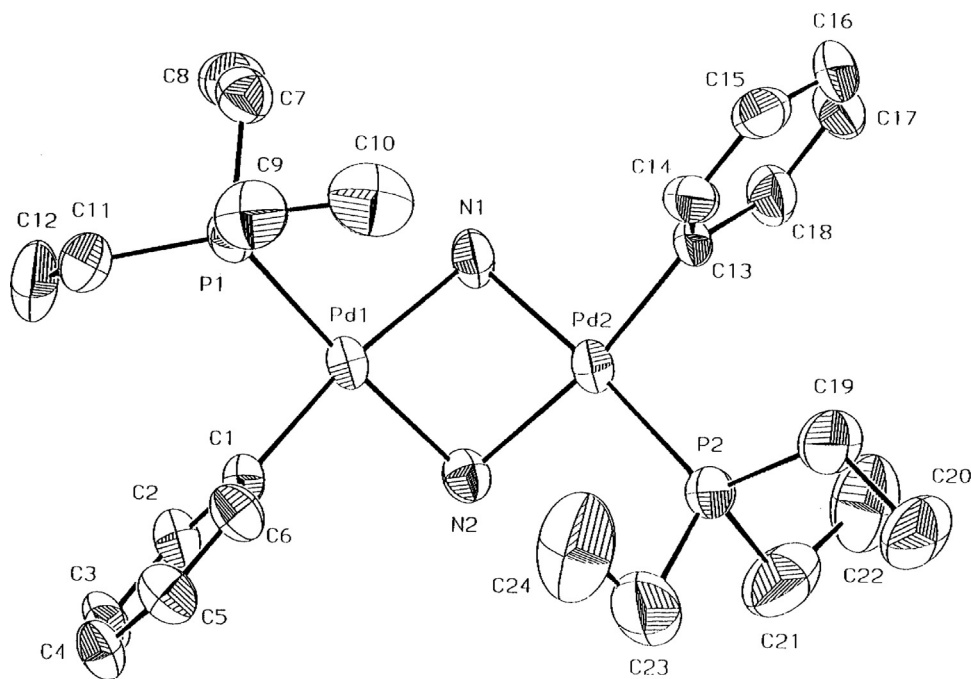


Fig. 1. The molecular structure for one of the two crystallographically independent molecules of **2** shown with 40% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.104(7), Pd(1)–N(2) 2.085(7), Pd(2)–N(1) 2.067(7), Pd(2)–N(2) 2.127(7), Pd(1)–C(1) 2.000(9), Pd(2)–C(13) 1.998(9), Pd(1)–P(1) 2.233(3), Pd(2)–P(2) 2.235(3); Pd(2)–N(1)–Pd(1) 90.4(3), Pd(1)–N(2)–Pd(2) 89.3(3), N(2)–Pd(1)–N(1) 77.8(3), N(1)–Pd(2)–N(2) 77.7(3), C(1)–Pd(1)–N(2) 93.5(3), C(1)–Pd(1)–N(1) 171.3(3), C(1)–Pd(1)–P(1) 89.0(3), N(2)–Pd(1)–P(1) 174.3(2), N(1)–Pd(1)–P(1) 99.5(2), C(13)–Pd(2)–N(1) 92.8(3), C(13)–Pd(2)–N(2) 170.4(3), C(13)–Pd(2)–P(2) 91.7(3), N(1)–Pd(2)–P(2) 175.1(2), N(2)–Pd(2)–P(2) 97.7(2).

the diastereospecific insertion derivative of Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(CR = CR(NH₂)) (R = CO₂Me (**6a**), CO₂Et (**6b**)) (Scheme 3). Complexes **6a** and **6b** have been fully characterized by multinuclear NMR (¹H, ¹³C, ³¹P) and FAB/MS spectroscopy. In solution, no coordination of the amino group in the complex has been observed, as evidenced by the ¹H and ³¹P{¹H} NMR spectroscopy; all signals were intact on addition of coordinating molecules such as pyridine and PPh₃ to the *d*₆-benzene solution of **6a** and **6b**. An attempt at isolation of complexes **6a** and **6b** was unsuccessful due to their high solubility in most organic solvents including *n*-pentane. Thus, removal of all volatiles from the solution under high vacuum resulted in yellow solids that afforded satisfactory FAB/MS spectroscopic data, displaying a parent molecular ion peak in good accordance with the calculated molecular weight in addition to the expected peaks due to molecular fragmentation. Although the absolute diastereomeric configuration of **6a** and **6b** could not be determined owing to failure of obtaining suitable crystals for an X-ray structural study, we assigned the stereochemistry of complexes **6a** and **6b** (*Z*)-isomer by performing subsequent reactions. A further reaction of **6a** and **6b** with an acidic phenol HOC₆H₄-*p*-NO₂ produced only a single isomeric product *cis*-CHR = CR(NH₂) (R = CO₂Me (**7a**), CO₂Et (**7b**)) with retention of configuration, along with the palladium(II) *p*-nitrophenoxide Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (**8**) (Scheme 3) (see Experimental section). For a control, reacting a *d*₆-benzene solution of dialkyl acetylenedicarboxylate with ammonia produces an isomeric mixture of *cis*- and *trans*-(CHR = CR(NH₂)) (see Experimental section). The

diastereoselective formation of (*Z*)-Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(CR = CR(NH₂)) (**6a**, **6b**) resulted from the reaction of Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₂) (**4**) and RC≡CR implies that the insertion reaction presumably involves a concerted pathway, apparently ruling out a dissociative nucleophilic addition. In view of the importance of utilizing ammonia as a substrate for the production of nitrogen-containing compounds [6], this study on the reaction profile for *syn*-insertion of activated acetylene into the Pd–NH₂ bond in the title complex is noteworthy. Rare examples of *syn*-insertion of alkynes and alkenes into the Pd–N bonds have mostly been found in arylamido complexes [13]. Prior study on reaction of *trans*-Pd(PMe₃)₂(C₆H₅)(NHPH) with DMAD described *syn*-insertion of the C≡C triple bond into the Pd–NHPH bond to yield *trans*-Pd(PMe₃)₂(C₆H₅)((MeO₂C)C = C(CO₂Me)(NHPH)) [13a]. Inter- and intra-molecular *syn*-migratory insertion of alkenes into the Pd(II)-arylamido bonds in Pd(*o*-CH₂P(*t*-Bu)₂C₆H₄)(THF)(NR₂) [13b] and (dppf)(C₆H₄F-*p*)Pd(N(C₆H₄F-*p*))(CH₂)₃CH = CH₂) [13c], respectively, have also been demonstrated.

The formation of Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (**8**) generated from reaction of the vinyl complex (**6a**, **6b**) and HOC₆H₄-*p*-NO₂ has been verified by its independent synthesis from reaction of Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OTf) and Na(OC₆H₄-*p*-NO₂) in THF. The observed reactivity for the palladium(II) vinyl complexes toward HOC₆H₄-*p*-NO₂ in the ligand exchange reaction reveals that the σ -vinylic ligand is more basic than the σ -phenoxide in the complexes, liberating stereoselective olefin derivatives with retention of configuration. The reaction of complex **4** with an activated olefin such as

acrylonitrile was attempted, without giving a clean insertion product, instead producing polymeric species of acrylonitrile which precipitates in solution. The isolated polymer shows its characteristic absorption peaks for the $\nu(\text{CN})$ at 2245 and 2204 cm^{-1} in the IR spectrum. No reaction of **4** with unactivated olefins such as 1-hexene and cyclohexene was observed, being presumably ascribed to an insufficient nucleophilicity of the coordinated amide along with the rigidity of the sterically hindered pincer ligand.

3. Conclusion

We have prepared novel parent-amido complexes of palladium(II) with bridging and terminal NH_2 . The monomeric palladium(II) amide $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NH}_2)$ undergoes nucleophilic addition with activated acetylene $\text{RC}\equiv\text{CR}$ ($\text{R} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$) to yield diastereospecific vinyl complex $(Z)\text{-Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{CR} = \text{CR}(\text{NH}_2))$. The produced vinyl complexes react with $\text{HOC}_6\text{H}_4\text{-}p\text{-NO}_2$ to give $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{OC}_6\text{H}_4\text{-}p\text{-NO}_2)$ along with olefin derivatives $\text{cis-CHR} = \text{CR}(\text{NH}_2)$ with retention of the diastereomeric configuration. The title complexes along with their reaction profiles toward the $\text{C}\equiv\text{C}$ triple bond may provide useful information relevant to catalytic functionalization of unsaturated hydrocarbons with ammonia. Further study on catalytic hydroamination of unsaturated hydrocarbons with ammonia in the presence of the title complexes is currently underway.

4. Experimental

4.1. General

All preparations of air-susceptible compounds were carried out on a standard Schlenk line or in a glovebox under argon. PdCl_2 was supplied by Kojima Chemicals Co., Ltd., and used without purification. AgOTf , dppe , α, α' -dibromo-*m*-xylene, CDCl_3 and C_6D_6 were purchased from Aldrich Chemical Company, and used as supplied. Dicyclohexylphosphine was supplied by Strem Chemicals Inc. All other reagents were from various commercial companies. $[\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NH}_3)]\text{OTf}$ and $\text{trans-}[\text{Pd}(\text{PEt}_3)_2(\text{Ph})(\text{NH}_3)]\text{OTf}$ were prepared according to the literature [14]. IR spectra were recorded on a Bruker (Tensor 37) FT-IR spectrometer, as a pressed KBr pellets. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured on a Varian Gemini-2000 spectrometer. GC/MS analyses were carried out using an HP 6890 gas chromatograph equipped with an HP 5973 MSD and an HP-Ultra 1 column. FAB/MS and Elemental analyses were performed at Korea Basic Science Institute in Seoul, Korea.

4.2. Synthesis and reactions

4.2.1. Synthesis of anti- $[\text{Pd}(\text{Ph})(\text{PEt}_3)(\mu\text{-NH}_2)]_2$ (**2**)

In a glovebox under argon atmosphere, a mixture of $\text{trans-}[\text{Pd}(\text{PEt}_3)_2(\text{Ph})(\text{NH}_3)]\text{OTf}$ (500 mg, 0.85 mmol) and NaNH_2 (150 mg, 3.8 mmol) was stirred in THF (20 mL) for 6 h at ambient temperature. Color of the reaction suspension was slowly changed from light grey to deep grey during the course of the reaction. The resulting suspension

was filtered under vacuum to give a pale yellow solution. Removal of all volatiles from the filtrate under high vacuum resulted in yellow residues that were extracted with *n*-pentane (4×10 mL) to give a pale yellow solution. The volume of solution was reduced to ca. 10 mL to slowly give a colorless precipitates that were filtered, washed with cold *n*-pentane, and dried *in vacuo*. Yield 176 mg (65%). IR (KBr): $\nu(\text{NH}) = 3238, 3367 \text{ cm}^{-1}$ (w, br). $^1\text{H NMR}$ (C_6D_6): $\delta -1.35$ br (4H, NH_2), $\delta 0.93$ m (18H, CH_3), $\delta 1.09$ m (12H, CH_2), $\delta 7.08$ t (2H, *p*-CH (Ph), $^3J(\text{HH}) = 7.3$ Hz), $\delta 7.26$ t (4H, *m*-CH (Ph), $^3J(\text{HH}) = 7.3$ Hz), $\delta 7.78$ d (4H, *o*-CH (Ph), $^3J(\text{HH}) = 7.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 8.22$ s (CH_3), $\delta 15.61$ d (CH_2 , $^1J(\text{CP}) = 26.7$ Hz), $\delta 122.3$, $\delta 127.1$, $\delta 137.6$. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 20.2$ s. Anal. Calcd for $\text{C}_{24}\text{H}_{44}\text{N}_2\text{P}_2$: C, 45.4; H, 6.98; N 4.41. Found: C, 45.1; H, 6.84; N, 4.20.

4.2.2. Synthesis of $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NH}_2)$ (**4**)

At a similar reaction condition as for complex **2**, a mixture of $[\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NH}_3)]\text{OTf}$ (500 mg, 0.65 mmol) and NaNH_2 (100 mg, 2.6 mmol) was stirred in THF (30 mL). The color of the reaction mixture was slowly changed from light grey to red during the course of the reaction. After 4 h, the resulting mixture was filtered under vacuum to give a red solution. Removal of all volatiles from the filtrate under high vacuum resulted in deep-red residues that were extracted with *n*-hexane (4×5 mL) to give a pale yellow solution. Removal of solvent from the extracted solution under high vacuum gave spectroscopically pure compound of $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NH}_2)$. Yield 270 mg (68%). Spectral data for $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NH}_2)$ (**4**): $^1\text{H NMR}$ (C_6D_6): $\delta -0.20$ br (2H, NH_2), $\delta 1.0\text{--}2.4$ m (44H, Cy), $\delta 3.10$ vt (4H, CH_2 , $^2J(\text{PH}) + ^4J(\text{PH}) = 8.4$ Hz), $\delta 7.08$ m (3H, CH(aryl)). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 50.7$ s.

4.2.3. Reaction of $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NH}_2)$ (**4**) with dialkyl acetylenedicarboxylate ($\text{RC}\equiv\text{CR}$; $\text{R} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$) to yield $(Z)\text{-Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{CR} = \text{CR}(\text{NH}_2))$ ($\text{R} = \text{CO}_2\text{Me}$ (**6a**), CO_2Et (**6b**))

To a d_6 -benzene (0.3 mL) solution of **4** (15 mg, 0.024 mmol) in a 5-mm screw-capped NMR tube (Wilmad, 528-TR) was added a slight excess of dialkyl acetylenedicarboxylate ($\text{RC}\equiv\text{CR}$; $\text{R} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$; 0.032 mmol, 0.1 mL of a diluted d_6 -benzene solution that was prepared by the addition of DMAD (46 mg) or DEAD (54 mg) into 1.0 mL of d_6 -benzene). The insertion product $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{CR} = \text{CR}(\text{NH}_2))$ was quantitatively formed from the reaction, which was monitored by NMR spectroscopy. The product can hardly be isolated from the solution because of the high solubility in most organic solvents. Thus, the removal of all volatiles from the solution under high vacuum resulted in yellow solids that afforded satisfactory FAB/MS spectroscopic data. For $\text{Pd}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)((\text{MeO}_2\text{C})\text{C} = \text{C}(\text{CO}_2\text{Me})(\text{NH}_2))$ (**6a**): $^1\text{H NMR}$ (C_6D_6): $\delta 1.0\text{--}2.4$ m (44H, Cy), $\delta 3.49$ s (3H, CH_3), $\delta 3.73$ s (3H, CH_3), $\delta 3.10$ dt (H_a, CH_2 ; $^2J(\text{H}_a\text{H}_b) = 17.6$ Hz, $^2J(\text{PH}) + ^4J(\text{PH}) = 7.9$ Hz), $\delta 3.31$ dt (H_b, CH_2 ; $^2J(\text{H}_a\text{H}_b) = 17.6$ Hz, $^2J(\text{PH}) + ^4J(\text{PH}) = 7.9$ Hz), $\delta 3.89$ br (2H, NH_2), $\delta 7.21$ m (3H, CH (aryl)). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 50.53$, $\delta 51.45$ s (CO_2CH_3), $\delta 162.08$, $\delta 176.40$ (CO_2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 51.7$ s. FAB/MS: observed

m/z 761.22. Calcd for $C_{38}H_{59}NO_4P_2Pd$, 761.30. For $Pd(2,6-(Cy_2PCH_2)_2C_6H_3)((EtO_2C)C=C(CO_2Et)(NH_2))$ (**6b**): 1H NMR (C_6D_6): δ 1.0–2.4 m (44H, Cy), δ 1.08 t (3H, CH_3 , $^3J(HH) = 7.1$ Hz), δ 1.34 t (3H, CH_3 , $^3J(HH) = 7.1$ Hz), δ 4.12 q (2H, CH_2 , $^3J(HH) = 7.1$ Hz), δ 4.31 q (2H, CH_2 , $^3J(HH) = 7.1$ Hz), δ 3.10 dt (H_a, CH_2 ; $^2J(H_aH_b) = 17.6$ Hz, $^2J(PH) + ^4J(PH) = 8.3$ Hz), δ 3.30 dt (H_b, CH_2 ; $^2J(H_aH_b) = 17.6$ Hz, $^2J(PH) + ^4J(PH) = 8.3$ Hz), δ 3.94 br (2H, NH_2), δ 7.21 m (3H, $CH(aryl)$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.47, δ 15.15 ($CO_2CH_2CH_3$), δ 58.98, δ 60.30 ($CO_2CH_2CH_3$), δ 162.08, δ 176.09 ($CO_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51.9 s. FAB/MS: observed m/z 789. 25. Calcd for $C_{40}H_{63}NO_4P_2Pd$, 789. 33.

4.2.4. Reaction of (Z)-Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(CR = CR(NH₂))(R = CO₂Me (6a**), CO₂Et (**6b**)) with HOC₆H₄-*p*-NO₂ to yield *cis*-CHR = CR(NH₂) (R = CO₂Me (**7a**), CO₂Et (**7b**)) and Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (**8**)**

To a d_6 -benzene (0.3 mL) solution of **6a** or **6b** (ca. 15 mg) in a 5-mm screw-capped NMR tube was added HOC₆H₄-*p*-NO₂ (5 mg). The reaction proceeded quantitatively to produce *cis*-CHR = CR(NH₂) (R = CO₂Me (**7a**), CO₂Et (**7b**)) and Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (**8**). All products were analyzed by 1H and ^{31}P NMR, and GC/mass spectroscopy. The *p*-nitrophenoxide complex Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (**8**) can be independently prepared through an equimolar reaction of Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OTf) and NaOC₆H₄-*p*-NO₂ in THF. For *cis*-((MeO₂C)CH = C(CO₂Me)(NH₂)) (**7a**): 1H NMR (C_6D_6): δ 3.15 s (3H, CH_3), δ 3.44 s (3H, CH_3), δ 5.77 s (1H, CH). GC/MS: $m/z = 159, 128, 100, 68, 59$. Calcd for $C_6H_9NO_4$, 159.05. For *cis*-((EtO₂C)CH = C(CO₂Et)(NH₂)) (**7b**): 1H NMR (C_6D_6): δ 0.78 t (3H, CH_3 , $^3J(HH) = 7.13$ Hz), δ 1.02 t (3H, CH_3 , $^3J(HH) = 7.13$ Hz), δ 3.79 q (2H, CH_2 , $^3J(HH) = 7.13$ Hz), δ 4.07 q (2H, CH_2 , $^3J(HH) = 7.13$ Hz), δ 5.84 s (1H, CH). GC/MS: $m/z = 187, 142, 114, 86, 68$. Calcd for $C_8H_{13}NO_4$, 187.08. For Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (**8**): IR (KBr): $\nu(NO) = 1583, 1303$ cm^{-1} (sh, s). 1H NMR (C_6D_6): δ 0.9–2.1 m (44H, Cy), δ 2.84 vt (4H, CH_2 , $^2J(PH) + ^4J(PH) = 8.4$ Hz), δ 6.88 d (2H, $^3J(HH) = 9.2$ Hz), δ 8.49 d (2H, $^3J(HH) = 9.2$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 50.7 s. Anal. Calcd for $C_{38}H_{55}NO_3P_2Pd$: C, 61.5; H, 7.47; N 1.89. Found: C, 61.1; H, 7.52; N, 1.58.

4.2.5. Reaction of **4 with [Ph₂I](SO₃CF₃) or [Ph₂I]Cl**

To a d_6 -benzene (0.3 mL) solution of **4** (15 mg) in a 5-mm screw-capped NMR tube was added a slight excess amount of [Ph₂I]SO₃CF₃. The reaction produced a cationic aniline complex [Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(NH₂Ph)]OTf, which was confirmed by its independent preparation from the reaction of Pd(2,6-(Cy₂PCH₂)₂C₆H₃)OTf and NH₂Ph, showing the identical ^{31}P NMR resonance at δ 52.1 in d_6 -benzene. An attempt to isolate the cationic aniline species was unsuccessful due to the dissociation of the coordinated aniline converting to Pd(2,6-(Cy₂PCH₂)₂C₆H₃)(OTf) ($^{31}P\{^1H\}$ NMR (C_6D_6): δ 54.5). In the meantime, reaction of **4** with [Ph₂I]Cl produced Pd(2,6-(Cy₂PCH₂)₂C₆H₃)Cl ($^{31}P\{^1H\}$ NMR (C_6D_6): δ 52.3) along with the liberation of NH₂Ph (GC/MS: $m/z = 93, 66, 39$).

4.2.6. Reaction of dialkyl acetylenedicarboxylate with ammonia

Anhydrous ammonia gas was bubbled into a d_6 -benzene (0.3 mL) solution of dialkyl acetylenedicarboxylate (DMAD, DEAD; ca. 20 mg, respectively) for ca. 30 s in a 5-mm screw-capped NMR tube. The reaction produced an isomeric mixture of *cis*- and *trans*-(CHR = CR(NH₂)) in a ratio of *trans/cis* = ca. 1.3. For *trans*-((MeO₂C)CH = C(CO₂Me)(NH₂)): 1H NMR (C_6D_6): δ 3.42 s (3H, CH_3), δ 3.59 s (3H, CH_3), δ 4.80 s (1H, CH). For *trans*-((EtO₂C)CH = C(CO₂Et)(NH₂)): 1H NMR (C_6D_6): δ 0.75 t (3H, CH_3 , $^3J(HH) = 7.13$ Hz), δ 1.01 t (3H, CH_3 , $^3J(HH) = 7.13$ Hz), δ 3.37 q (2H, CH_2), δ 4.08 q (2H, CH_2), δ 4.90 s (1H, CH). For *cis*-((MeO₂C)CH = C(CO₂Me)(NH₂)) and *cis*-((EtO₂C)CH = C(CO₂Et)(NH₂)): refer to [Experimental section](#), § 4.2.4.

Acknowledgements

This work was supported by the Dongguk University Research Fund of 2013. The authors are grateful to Prof. M.S. Lah for an X-ray diffraction study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2015.05.007>.

References

- (a) M.D. Fryzuk, C.D. Montgomery, *Coord. Chem. Rev.* 95 (1989) 1; (b) H.E. Brynza, W. Tam, *Chem. Rev.* 88 (1988) 1163; (c) J.R. Fulton, A.W. Holland, D.J. Fox, R.G. Bergman, *Acc. Chem. Res.* 35 (2002) 44; (d) J.F. Hartwig, *Nature* 455 (2008) 314; (e) J.P. Wolfe, S. Wagaw, J.F. Marcoux, S.L. Buchwald, *Acc. Chem. Res.* 31 (1998) 805.
- (a) A.L. Casalnuovo, J.C. Calabrese, D. Milstein, *J. Am. Chem. Soc.* 110 (1988) 6738; (b) R.L. Cowan, W.C. Troglor, *J. Am. Chem. Soc.* 111 (1989) 4750; (c) J.F. Hartwig, R.G. Bergman, R.A. Andersen, *J. Am. Chem. Soc.* 113 (1991) 6499; (d) G.C. Martin, G.J. Palenik, J.M. Boncella, *Inorg. Chem.* 29 (1990) 2027; (e) A.L. Seligson, R.L. Cowan, W.C. Troglor, *Inorg. Chem.* 30 (1991) 3371; (f) Y.-W. Ge, F. Peng, P.R. Sharp, *J. Am. Chem. Soc.* 112 (1990) 2632; (g) C. Ye, P.R. Sharp, *Inorg. Chem.* 34 (1995) 55; (h) M.J. Fernandez, J. Modrego, F.J. Lahoz, J.A. López, L.A. Oro, *J. Chem. Soc., Dalton Trans.* (1990) 2587; (i) M.K. Kolel-Veetil, A.L. Rheingold, K.J. Ahmed, *Organometallics* 12 (1993) 3439; (j) J.-J. Brunet, G. Commenges, D. Neibecker, K. Philippot, L. Rosenberg, *Inorg. Chem.* 33 (1994) 6373; (k) Y.-J. Kim, J.-C. Choi, K. Osakada, *J. Organomet. Chem.* 491 (1995) 97; (l) J. Ruiz, M.T. Martinez, C. Vicente, G. Garcia, G. Lopez, P.A. Chaloner, P.B. Hitchcock, *Organometallics* 12 (1993) 4321; (m) J.F. Hartwig, *J. Am. Chem. Soc.* 118 (1996) 7010; (n) M.S. Driver, J.F. Hartwig, *J. Am. Chem. Soc.* 118 (1996) 4206; (o) D.D. VanderLende, K.A. Abboud, J.M. Boncella, *Inorg. Chem.* 34 (1995) 5319; (p) P.L. Holland, R.A. Andersen, R.G. Bergman, *J. Am. Chem. Soc.* 118 (1996) 1092; (q) J.V. Cuevas, G. Garcia-Herbosa, A. Munoz, S. Garcia-Granda, D. Miguel, *Organometallics* 16 (1997) 2220; (r) H. Matsuzaka, K. Ariga, H. Kase, T. Kamura, M. Kondo, S. Kitagawa, M. Yamasaki, *Organometallics* 16 (1997) 4514; (s) J.J. Li, W. Li, A.J. James, T. Holbert, T.P. Sharp, P.R. Sharp, *Inorg. Chem.* 38

- (1999) 1563;
 (t) U. Anandhi, T. Holbert, D. Lueng, P.R. Sharp, *Inorg. Chem.* 42 (2003) 1282;
 (u) A. Singh, U. Anandhi, M.A. Cinellu, P.R. Sharp, *Dalton Trans.* (2008) 2314;
 (v) J.F. Hartwig, *Inorg. Chem.* 46 (2007) 1936;
 (w) C. Munro-Leighton, Y. Feng, J. Zhang, N.M. Alsop, T.B. Gunnoe, P.D. Boyle, J.L. Petersen, *Inorg. Chem.* 47 (2008) 6124;
 (x) J.R. Webb, C. Munro-Leighton, A.W. Pierpont, J.T. Gurkin, T.B. Gunnoe, T.R. Cundari, M. Sabat, J.L. Petersen, P.D. Boyle, *Inorg. Chem.* 50 (2011) 4195.
- [3] (a) I. Mena, E.A. Jaseer, M.A. Casado, P. Garcia-Orduna, F.J. Lahoz, L.A. Oro, *Chem. Eur. J.* 19 (2013) 5665;
 (b) A.L. Casalnuovo, J.C. Calabrese, D. Milstein, *Inorg. Chem.* 26 (1987) 973;
 (c) F.P. Rotzlinger, W. Marty, *Inorg. Chem.* 22 (1983) 3593;
 (d) M. Kretschmer, L.Z. Heck, *Anorg. Allg. Chem.* 490 (1982) 215;
 (e) N.J. Curtis, K.S. Hagen, A.M. Sargeson, *Inorg. Chem.* 23 (1984) 1571;
 (f) L. Heck, M. Ardon, A. Bino, J. Zaap, *J. Am. Chem. Soc.* 110 (1988) 2691.
- [4] (a) G.C. Dobinson, R. Mason, G.B. Robertson, R.U.F. Conti, D. Morelli, S. Cenini, F. Bonati, *J. Chem. Soc., Chem. Comm.* (1967) 739;
 (b) N.W. Alcock, P. Bergamini, T.J. Kemp, P.G. Pringle, S. Sostero, O. Traverso, *Inorg. Chem.* 30 (1991) 1594;
 (c) C.A. O'Mahoney, I.P. Parkin, D.J. Williams, J.D. Woollins, *Polyhedron* 8 (1989) 1979.
- [5] (a) S. Park, A.L. Rheingold, D.M. Roundhill, *Organometallics* 10 (1991) 615;
 (b) F.L. Joslin, M.P. Johnson, J.T. Magee, D.M. Roundhill, *Organometallics* 10 (1991) 2781;
 (c) R. Koelliker, D. Milstein, *J. Am. Chem. Soc.* 113 (1991) 8524;
 (d) D.J. Fox, R.G. Bergman, *Organometallics* 23 (2004) 1656;
 (e) D. Conner, K.N. Jayaprakash, T.R. Cundari, T.B. Gunnoe, *Organometallics* 23 (2004) 2724;
 (f) D.V. Gutsulyak, W.E. Piers, J. Borau-Garcia, M. Parvez, *J. Am. Chem. Soc.* 135 (2013) 11776;
 (g) Y.-H. Chang, Y. Nakajima, H. Tanaka, K. Yoshizawa, F. Ozawa, *J. Am. Chem. Soc.* 135 (2013) 11791.
- [6] (a) J.I. van der Vlugt, *Chem. Soc. Rev.* 39 (6) (2010) 2302;
 (b) D.M. Roundhill, *Chem. Rev.* 92 (1992) 1;
 (c) G.D. Vo, J.F. Hartwig, *J. Am. Chem. Soc.* 131 (2009) 11049;
 (d) D.S. Surry, S.L. Buchwald, *J. Am. Chem. Soc.* 129 (2007) 10354;
 (e) T. Schulz, C. Torborg, S. Enthaler, B. Schaffner, A. Dumrath, A. Spannenberg, H. Neumann, A. Borner, M. Beller, *Chem. Eur. J.* 15 (2009) 4528;
 (f) R.J. Lundgren, A. Sapping-Kumankumah, M. Stradiotto, *Chem. Eur. J.* 16 (2010) 1983.
- [7] (a) Q. Shen, J.F. Hartwig, *J. Am. Chem. Soc.* 128 (2006) 10028;
 (b) J.L. Klinkenberg, J.F. Hartwig, *J. Am. Chem. Soc.* 132 (2010) 11830.
- [8] (a) J.M. Seul, S. Park, *J. Chem. Soc. Dalton Trans.* (2002) 1153;
 (b) S.Y. Ryu, H. Kim, H.S. Kim, S. Park, *J. Organomet. Chem.* 592 (1999) 194;
 (c) J.M. Seul, S. Park, *Bull. Korean Chem. Soc.* 31 (2010) 3745.
- [9] Crystal data for **2**: C₂₄H₄₄N₂P₂Pd₂, MW = 635.41, colorless prism with dimensions (0.8 × 0.50 × 0.25 mm), monoclinic, space group P2₁/n, a = 13.228(2), b = 18.132(2), c = 24.745(2) Å, β = 101.410(10), V = 5818(1) Å³, Z = 4, F(000) = 2688, T = 293(2) K, 2.02 ≤ θ ≤ 22.56°, μ(Mo Kα) = 1.360 mm⁻¹, 7990 reflections collected, 7614 [R(int) = 0.0373] independent reflections, λ(Mo Kα) = 0.71069 Å. Refinement on F² was carried out by full-matrix least-squares methods. Data/restraints/parameters = 7613/0/540, goodness-of-fit on F² = 1.122, R₁(wR₂) = 0.0547(0.1417) for final R indices [I > 2σ(I)], R₁(wR₂) = 0.0715(0.1504) for all data, A final difference Fourier showed no residual density outside 0.743 and -0.717 e-Å⁻³.
- [10] K.R. Dixon, A.C. Dixon, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 9, Pergamon, Oxford, 1994, p. 196.
- [11] (a) L.A. Villanueva, K.A. Abboud, J.M. Boncella, *Organometallics* 13 (1994) 3921;
 (b) J. Ruiz, V. Rodriguez, G. Lopez, P.A. Chaloner, P.B. Hitchcock, *J. Chem. Soc. Dalton Trans.* *Inorg. Chem.* 22 (1997) 4271;
 (c) J. Ruiz, V. Rodriguez, G. Lopez, J. Casabo, E. Molins, C. Miravittles, *Organometallics* 18 (1999) 1177.
- [12] (a) H.-W. Suh, T.J. Schmeier, N. Hazari, R.A. Kemp, M.K. Takase, *Organometallics* 31 (2012) 8225;
 (b) C.J. Moulton, B.L. Shaw, *J. Chem. Soc. Dalton Trans.* (1976) 1020.
- [13] (a) L.A. Villanueva, K.A. Abboud, J.M. Boncella, *Organometallics* 11 (1992) 2963;
 (b) P.S. Hanley, D. Marković, J.F. Hartwig, *J. Am. Chem. Soc.* 132 (2010) 6302;
 (c) J.D. Neukom, N.S. Perch, J.P. Wolfe, *J. Am. Chem. Soc.* 132 (2010) 6276.
- [14] J.G. Yun, J.M. Seul, K.D. Lee, S. Kim, S. Park, *Bull. Korean Chem. Soc.* 17 (1996) 311.